1. Obtain the expression for the total differential $dP$ for a van der Waals gas in terms of $dT$ and $dV_m$.

**Solution**

The van der Waals equation of state is:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Since we have $P = P(V_m, T)$, the total differential is

$$dP = \left(\frac{\partial P}{\partial T}\right)_p dT + \left(\frac{\partial P}{\partial V_m}\right)_T dV_m$$

We can evaluate each of the partial derivatives in the total differential:

$$\left(\frac{\partial P}{\partial T}\right)_p = \frac{\partial}{\partial T} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)$$

$$= \frac{R}{V_m - b}$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = \frac{\partial}{\partial V_m} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)$$

$$= -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$$

Now we can substitute these back into the total differential expression to get:

$$dP = \left(\frac{R}{V_m - b}\right) dT + \left(\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2}\right) dV_m$$

2. Determine the thermal expansion coefficient $\alpha$ for a gas that obeys the van der Waals equation of state. (Hint: try using the cyclic rule for partial derivatives to express the thermal expansion coefficient in terms of more convenient quantities)

**Solution**

To evaluate $\alpha$, we need the partial derivative $\left(\frac{\partial V_m}{\partial T}\right)_P$. Unfortunately, the van der Waals equation of state cannot be explicitly solved for $V_m$. However, we can use the properties of partial derivatives to calculate the desired quantity indirectly. Start by using the cyclic relationship:

$$\left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial V_m}\right)_T \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Solve for the desired partial derivative (in red):

$$\left(\frac{\partial V_m}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V_m}{\partial P}\right)_T$$

↓ write the first partial derivative (in blue) in terms of its reciprocal

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V_m}\right)_T}$$

Now the desired partial derivative is in terms of the partial derivatives that we already calculated in problem #1. Substitution of these expressions gives:

$$\left(\frac{\partial V_m}{\partial T}\right)_V = -\frac{R}{(V_m - b)}$$

$$\left(\frac{\partial V_m}{\partial V_m}\right)_T = \frac{2a}{V_m^3} - \frac{RT}{V_m^3 (V_m - b)^2}$$

↓ combine the terms in the denominator (continued on next page)
3. Calculate the molar volume of chlorine gas at 350 K and 2.30 atm using (a) the ideal gas law and (b) the van der Waals equation. For (b), you cannot solve the van der Waals equation explicitly for the molar volume. However, you can use the answer from (a) as a first approximation to the molar volume term on the right hand side and then use successive approximations to obtain a numerical answer for (b). Use $a = 6.26 \text{L atm mol}^{-2}$ and $b = 5.42 \times 10^{-2} \text{L mol}^{-1}$.

**Solution**

a. For an ideal gas, the molar volume is

$$V_m = \frac{RT}{P}$$

\[\downarrow \text{be sure to use the value of } R \text{ with the correct units!}\]

\[= \frac{(8.206 \times 10^{-2} \text{L atm K}^{-1} \text{mol}^{-1})(350K)}{2.30 \text{atm}} = 12.5 \text{L mol}^{-1}\]

b. Rearrange the van der Waals equation to solve for the molar volume:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

\[\downarrow \]

$$V_m = \frac{RT}{P + \frac{a}{V_m^2}} + b$$

Substitute the molar volume from part (a) into the molar volume on the right hand side of the above equation (the term in red):

$$V_m = \frac{(8.206 \times 10^{-2} \text{L atm K}^{-1} \text{mol}^{-1})(350K)}{(2.30 \text{atm}) + \frac{6.260 \text{L atm mol}^{-2}}{(12.5 \text{L mol}^{-1})^2}} + 5.42 \times 10^{-2} \text{L mol}^{-1}$$

$$= 12.3 \text{ L mol}^{-1}$$

Substitution of this result (12.3 L mol$^{-1}$) into the first approximation gives 12.3 L mol$^{-1}$, which means that the cycle of approximation has converged and can be terminated.
4. The compression factor for a gas, $Z$, is a measure of the deviation from ideal behavior. However, it can also be used to relate the properties of different gases. (a) Derive an expression for the compression factor for a van der Waals gas. (b) Express the result in (a) as a virial expansion in powers of $1/V_m$ and (c) obtain expressions for $B$ and $C$ in terms of the van der Waals parameters $a$ and $b$ and calculate their values. The expansion you will need is

$$\frac{1}{1-x} = 1 + x + x^2 + \ldots$$

Measurements on argon at 273 K gave the following virial coefficients:

$B = -21.7 \text{ cm}^3 \text{ mol}^{-1}$

$C = 1200 \text{ cm}^6 \text{ mol}^2$

**Solution**

a. Simply substitute the van der Waals equation into the expression for the compression factor and simplify:

$$Z = \frac{P V_m}{R T}$$

\[\downarrow\text{use the van der Waals equation for } P \text{ (in red)}\]

\[\left( \frac{1}{R T} \right) \left( \frac{RT - a}{V_m - b V_m^2} \right) V_m\]

\[\downarrow\text{simplify with a bit of algebra}\]

\[\left( \frac{1}{R T} \right) \left( \frac{V_m RT}{V_m - b V_m^2} - a \right)\]

\[= \frac{V_m}{V_m - b} - \frac{a}{RTV_m}\]

\[= \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}\]

b. The second term above is already in terms of $1/V_m$ and does not need to be expanded further. Expanding the first term gives:

$$\frac{1}{1 - \frac{b}{V_m}} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \ldots$$

Writing the expansion and including the second term from (a) gives:

$$\frac{P V_m}{R T} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} - \frac{a}{RTV_m}\]

\[= 1 + \left( \frac{b - \frac{a}{RT}}{V_m} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \ldots\]

Solve for $P V_m$:

$$P V_m = RT \left[ 1 + \left( \frac{b - \frac{a}{RT}}{V_m} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \ldots \right]$$

C. The virial coefficients $B$ and $C$ are determined by comparison with the virial equation of state. The virial equation is:

$$P V_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots \right)$$

Comparison with the result from (b) shows that:

$$B = b - \frac{a}{RT} \text{ and } C = b^2$$

Now we just solve for $a$ and $b$. For $a$ we have:

$$a = RT (b - B)$$

\[\downarrow\text{make the substitutions}\]
5. Show that 
\[ \lim_{P \to 0} \left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left( b - \frac{a}{RT} \right) \]
for a van der Waals gas in the ideal gas limit. Remember that \(1/V_m \to 0\) as \(P \to 0\). (comment: Don’t make this harder than it needs to be. Simply evaluate the derivative and take the necessary limit.)

**Solution**
Start by writing \( (\partial Z/\partial P)_T \) using the van der Waals equation for \( P \):
\[
(\frac{\partial Z}{\partial P})_T = \frac{\partial Z}{\partial Z} \left( \frac{RT}{V_m - b - \frac{a}{V_m^2}} \right)
\]
In the ideal gas limit \( V_m \to \infty \) so that:
\( V_m >> b \) and \( \frac{a}{V_m^2} \approx 0 \)
This means that we can drop the terms in red from the original expression:
\[
(\frac{\partial Z}{\partial P})_T = \left( \frac{\partial Z}{\partial Z} \right) \left( \frac{RT}{V_m} \right)
\]
\( R \) is a constant
\[ = \frac{1}{RT} \left( \frac{\partial Z}{\partial \frac{1}{V_m}} \right)_T \]

Now we use:
\[ \frac{1}{V_m^2} = - \frac{1}{V_m^2} dV_m \]
So that the expression becomes:
\[ (\frac{\partial Z}{\partial P})_T = -\frac{V_m^2}{RT} \left( \frac{\partial Z}{\partial V_m} \right)_T \]

Next, we recognize that
\[ Z = PV_m \]
\( \downarrow \) substitute the van der Waals equation for \( P = \frac{RT}{V_m - b - \frac{a}{V_m^2}} \)
\[ = V_m - b - \frac{a}{RTV_m} \]
Now we can substitute this for \( Z \) and evaluate the derivative:
\[ (\frac{\partial Z}{\partial P})_T = -\frac{V_m^2}{RT} \left[ \frac{\partial}{\partial V_m} \left( \frac{V_m}{V_m - b - \frac{a}{RTV_m}} \right)_T \right] \]
\[ = -\frac{V_m^2}{RT} \left[ \left( \frac{\partial}{\partial V_m} \left( \frac{V_m}{V_m - b} \right) \right)_T + \left( \frac{\partial}{\partial V_m} \left( \frac{a}{RTV_m} \right) \right)_T \right] \]
\( \downarrow \) continued on next page
6. Verify that the van der Waals, the virial, and the Redlich-Kwong equations all reduce to \( PV = NRT \) in the limit of zero density. (hint: remember that the density goes to zero as \( 1/V_m \to 0 \))

**Solution**

First, recognize that \( V_m \to \infty \) when \( 1/V_m \to 0 \). For the van der Waals equation, we start by noting that we can ignore \( b \) since \( b \ll V_m \). This leaves

\[
P = \frac{RT}{V_m} - \frac{a}{V_m^2}
\]

\[
= \frac{1}{V_m} \left( RT - \frac{a}{V_m} \right)
\]

\(
\downarrow \text{as } V_m \to \infty \text{ the second term in the parentheses goes to zero leaving the ideal gas equation}
\)

\[
\lim_{V_m \to \infty} \left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left( b - \frac{a}{RT} \right)
\]

The Redlich-Kwong equation is

\[
P = \frac{RT}{V_m} - \frac{a}{V_m (V_m + b) T^{1/2}}
\]

By the same argument, we can ignore \( b \) leaving

\[
P = \frac{RT}{V_m} - \frac{a}{V_m^{3/2} T^{1/2}}
\]

\[
\downarrow \text{as for the van der Waals equation, the second term in parentheses goes to zero, leaving the ideal gas equation}
\]

\[
\lim_{V_m \to \infty} \left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT}
\]

For the virial equation we have

\[
P V_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots \right)
\]

\(
\downarrow \text{as } V_m \to \infty \text{ the terms in parentheses go to zero (except 1 obviously) leaving the ideal gas equation}
\)

\[
= RT
\]